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FINAL TECHNICAL REPORT FOR CONTRACT N00014-81-C-0005:

POINT DEFECTS AND INTERFACES IN INSULATING SOLIDS

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The research summarized in this final technical report was supported under ONR contract N00014-81-C-0005 during the period 1 October 1980 to 31 August 1989. Included are (I) a brief summary of contract-period research accomplishments, and (II) a list of publications supported by the contract. Published papers and Ph.D. dissertations have been forwarded regularly to ONR as they have become available during the course of this contract.

I. SUMMARY OF RESEARCH ACCOMPLISHMENTS

A. Introduction

This contract was the latest phase in a long-standing relationship between ONR and the principal investigators on the experimental and theoretical study of silicon dioxide and the silicon - silicon dioxide interface. During this period we made important contributions towards understanding both bulk silicon dioxide and the interface, which has recently been called "the most important material system of our era[1]".

Our contributions have been severalfold. We (primarily Feigl and his students) carried out a number of experiments on MOS (metal-oxide-semiconductor) systems. These experiments were designed to study such important features as chlorine incorporation, hydrogen migration, interface trap generation, defect structures associated with fabrication conditions, and hysteresis effects associated with charge trapping at

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near-interface defects. This work was disseminated through a number of invited talks and review articles, including a 1986 article by Feigl in Physics Today[2].

In addition, we (primarily Fowler and his students) carried out theoretical studies on bulk oxide defects, including the peroxyl radical, the non-bridging oxygen hole center, and various E' centers. In the process we took the lead in applying the semiempirical molecular orbital technique MINDO/3 to such defects, which others are now following.

Within the past few years our experimental-theoretical interaction greatly strengthened because of (i) experiments involving tunneling to and from oxide defects near the interface with silicon, and (ii) a program of calculations on near-interface defects, using a model for the oxide due to Ourmazd. Thus as ONR support comes to an end, we have papers published and about to be published on (1) a new hysteretic tunneling model, based on tunneling followed by lattice relaxation; (2) detailed studies of E'-like centers in the oxide very close to the interface. We expect that the basic physics revealed in this work will be of considerable significance in further studies of this and other semiconductor-insulator interfaces.

B. Specific accomplishments

We summarize specific accomplishments by brief synopses of the Ph.D. research of the various students who worked on this project.

1. Arthur H. Edwards - Ph.D., Physics, 1981: Hole Centers in Silicon Dioxide. Present position: Associate Professor, Department of Electrical Engineering, University of North Carolina at Charlotte, Charlotte, NC.

Dr. Edwards applied the MINDO/3 molecular-orbital technique for the first time to defects in silicon dioxide. This pioneering work required the determination of certain parameters in the method, and involved the study of a variety of defects. His calculations on the peroxyl radical defect in amorphous silicon dioxide and its precursor resulted in the prediction of a form of that defect which has probably been observed in subsequent experiments. Edwards also studied other silicon dioxide defects, including E' centers and the nonbridging oxygen hole center. His collaboration with Fowler and Feigl continued after he left Lehigh and has led to several other publications on oxide defects, partially supported by this contract.

2. Stephen Titcomb - Ph.D., Physics, 1984: The Role of Chlorine in Oxide Charge Generation. Present position: Assistant Professor, Department of Electrical Engineering, University of Vermont.

Dr. Titcomb studied the role of Cl impurities in charge trapping phenomena in silicon dioxide films incorporated in MOS devices. He demonstrated that HCl and HCl-equivalent additives to the oxidizing ambient during dry oxidation of silicon have a significant effect on electron trapping and interface-state

generation during current transport across MOS devices. This effect is due to water produced in the high-temperature reaction of HCl and O_2, however, and is not due to the relatively large amount of Cl impurities incorporated in the oxide.

3. Richard Gale - Ph.D., Physics, 1985: Electron Currents in $Al/SiO_2/Si$ MOS Capacitors: Hydrogen Redistribution and Correlated Electrical Effects. Present position: Texas Instruments, Dallas, TX.

Dr. Gale studied the chemical and electrical effects of water contamination on $Al/SiO_2/Si$ MOS capacitors. Chemical analysis was performed using secondary ion mass spectrometry (SIMS). Hydrogen was found to be transported from the vicinity of the Al/SiO_2 interface under avalanche injection. No electronic transport of deuterium was observed, nor was electronic transport of hydrogen from the oxide bulk. Perhaps the most remarkable aspect of this work was the large accumulation of hydrogen in the oxide/silicon interface region, some spilling over into the silicon and causing boron acceptor deactivation.

4. Hongzong Chew - Ph.D., Physics, 1986: A Model for Interface State Generation during Charge Injection in $Al/SiO_2/Si$ Capacitors. Present position: AT&T Bell Laboratories, Allentown, PA.

Dr. Chew studied the basic electrical effects of electron trapping and interface state generation in conventional thermally grown oxide films. The charge trapped in the bulk and that trapped

at or near the interface were separately analyzed by a combination of photo I-V and high-low frequency C-V measurements. These results indicate that the bulk trapped charge was negative and the interface trapped charge was positive. Interface state generation under different injection techniques was also studied. Hydrogen transport effects were noted in Fowler-Nordheim (FN) injection. Hydrogen plays an important role in two suggested mechanisms for interface-state formation: in one case, it is suggested that Si-H bonds are broken by injected holes; in the second case, hydrogen atoms are thought to migrate from the bulk to the interface region, where they interact with strained bonds, leading to dangling bonds.

5. Jayanta Kumar Rudra - Ph.D., Physics, 1986: Oxygen- and Silicon-Vacancy and Hydrogen-Related Defects in Silicon Dioxide. Present position: Assistant Professor, Physics Department, Xavier University, New Orleans, LA.

Dr. Rudra used the MINDO/3 method to investigate a variety of defects in silicon dioxide. In the process he suggested and developed the first and only model for the E_2' center, a model which involves the displacement of a silicon atom from its normal position adjacent to an oxygen vacancy into an interstitial location, where it interacts with another oxygen. He further studied the E_1' center, developing a model featuring a similar silicon relaxation. He has continued to collaborate with us and has been involved in relaxation-energy calculations associated with the tunneling experiments of Zvanut, described below.

6. Mary Ellen Zvanut - Ph.D., Physics, 1988: The Development of Spectroscopic Techniques to Study Defects in Thin Film Silicon Dioxide. Present position: Postdoctoral research associate, Physics Department, University of North Carolina, Chapel Hill, NC.

Dr. Zvanut studied defects in thin film sputtered SiO_2 which is used as an optical coating material. C-V techniques were used to examine the properties of charge in an aluminum/sputtered oxide/native oxide/silicon capacitor. A hysteretic trapping behavior was found, similar to that observed in microelectronic grade oxide films. A band-to-trap tunneling model was developed based on the assumption that the defects were located at the native oxide-sputtered cxide interface. The central feature of this model, defect relaxation, provided a physical explanation for the hysteretic trapping behavior. These experiments were correlated with electron spin resonance experiments carried out at Ft. Monmouth. We continue to collaborate with Dr. Zvanut, and will shortly submit a theoretical paper in which the hysteretic tunneling is described in a manner analogous to the Franck-Condon effect in optical absorption.

7. Rakesh Sethi - Ph.D., Electrical Engineering, 1989: Charge Trapping and Transport in Ion-Sputtered Silicon Dioxide Thin Films. Present position: National Semiconductor, Santa Clara, CA.

Dr. Sethi studied the electrical properties of sputtered silicon dioxide thin films, including some of those studied by Dr. Zvanut. High electron trapping efficiencies were determined. The

location of trapped charge was found to be a strong function of applied field and temperature. Direct tunneling from silicon to traps in the oxide was observed with a time constant of order 0.5 sec. These films were found to exhibit good charge retention and endurance properties.

8. Andrew Chu - Ph.D. candidate, Physics: A Study of Oxide Defects Near the Si-SiO_2 Interface.

Mr. Chu is carrying out detailed calculations on oxide defects near the interface with silicon, using the MINDO/3 technique. These calculations are based on the tridymite oxide model of Ourmazd, although they are likely not tied to that model. Mr. Chu has investigated the stability of that model with respect to residual stresses. He has extended that model, noting the likely occurrence of an oxygen at a strained surface Si-Si bond. He has investigated in some detail the properties of oxide defects in both the first and second layer of the oxide. In the second layer the defects seem bulk-like in their properties, but in the first layer the oxide defect seems to "heal" and a broken bond occurs in the substrate silicon just below the interface. This work is in progress as Mr. Chu completes his Ph.D.

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